

## Fuel Processors for PEM Fuel Cells

*Levi Thompson (Primary Contact)*

*University of Michigan*

*Department of Chemical Engineering*

*3026 H.H. Dow Building*

*Ann Arbor, MI 48109-2136*

*Phone: (734) 647-7150; Fax: (734) 763-0459; E-mail: ltt@umich.edu*

*DOE Technology Development Manager: Valri Lightner*

*Phone: (202) 586-; Fax: (202) 586-9811; E-mail: Valri.Lightner@ee.doe.gov*

*Subcontractors:*

*Osram Sylvania, Towanda, Pennsylvania*

*Ricardo, Inc., Plymouth, Michigan*

### Objectives

- Demonstrate high performance desulfurizer, catalyst, micro-reactor and microcombustor/microvaporizer concepts that will enable production of compact fuel processors for proton exchange membrane (PEM) fuel cells
- Design, fabricate and evaluate a 1-kWe fuel-flexible fuel processor during the first 36 months (one of the fuels capable of being reformed will be EPA Phase II reformulated gasoline)
- Design, fabricate and evaluate a fuel-flexible fuel processor capable of producing up to 10 kWe hydrogen (one of the test fuels will be EPA Phase II reformulated gasoline)

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Startup/Transient Operation
- J. Durability
- M. Fuel Processor System Integration and Efficiency
- N. Costs

### Approach

- Tasks devised to accomplish the project objectives include:
- Design and model components and systems that would meet power density targets;
- Develop high capacity sorbents capable of removing sulfur to target levels;
- Develop better performing autothermal reforming (ATR), water gas shift (WGS) and preferential oxidation (PrOx) catalysts and associated microreactors;
- Fabricate highly efficient microcombustors/microvaporizers;
- Fabricate microchannel reactors and system;
- Evaluate components and fuel processing system;
- Estimate cost for fuel processor.

## Accomplishments

- Modeled several of the microchannel reactors (FEMLAB and FLUENT) and entire fuel processor system (ASPEN and Matlab Simulink);
- Demonstrated Cu-Y zeolite sorbents that significantly out-performed other available sorbents;
- Demonstrated ceria/zirconia-based ATR, carbide-based WGS and sol-gel derived PrOx catalysts that out-performed available commercial catalysts;
- Developed methods to scale up production of carbide-based catalysts;
- Designed fuel and water microvaporizers;
- Fabricated and tested metal, ceramic and silicon-based micro-reactors;
- Designed and began construction of prototype 1-kWe fuel processor system.

## Future Directions

During this coming year, our goal is to fabricate at least two 1-kWe fuel processor systems. The first design is a hybrid system that includes micro- and conventional reactor technologies. The second design will be based primarily on ceramic micro-reactors. Specific tasks will include:

- Fabricate highly efficient microcombustors/microvaporizers,
- Fabricate microchannel reactors and system,
- Evaluate components and fuel processing system.

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## Introduction

Fuel cells are being developed to power cleaner, more fuel efficient automobiles. The fuel cell technology favored by many automobile manufacturers is proton exchange membrane (PEM) cells operating with H<sub>2</sub> from liquid fuels like gasoline and diesel. A key challenge to the commercialization of PEM fuel cell based powertrains is the lack of sufficiently small and inexpensive fuel processors. Improving the performance and cost of the fuel processor will require the development of better performing catalysts, new reactor designs and better integration of the various fuel processing components. These components and systems could also find use in natural gas fuel processing for stationary, distributed generation applications.

## Approach

Prototype gasoline fuel processors will be produced and evaluated against the Department of Energy technical targets. Significant improvements over the present state-of-the-art will be achieved by integrating low-cost microchannel systems, high activity catalysts,  $\pi$ -complexation sorbents, and high

efficiency microcombustor/microvaporizers being developed at the University of Michigan. The microchannel system will allow (1) more efficient thermal coupling of the fuel processor components and minimization of the heat exchanger requirements, (2) improved catalyst performance due to optimal reactor temperature profiles and increased heat and mass transport rates, and (3) better cold-start and transient responses.

The project will be accomplished in 3 phases. The Phase I effort will focus on demonstrating compact desulfurizer, micro-reactor and microcombustor/microvaporizer components for a 1-kWe fuel processor, and developing low-cost methods for the production of microchannel systems. The components will be third-party tested and will provide the basis for design and fabrication of an integrated 1-kWe ethanol or gasoline fuel processor during Phase II. We will scale up the smaller processor to up to 10 kWe during Phase III.

## Results

**Design and modeling.** The modeling activities have been at three levels: detailed component modeling, modeling for simplified component integration and

thermal management, and system integration and optimization modeling. FLUENT is being applied to develop detailed computational fluid dynamics (CFD) models of the internal reacting flow process for the prototype reactor components. The results are being used to design the ATR, WGS and PrOx reactors. A general 1-D counterflow heat exchanger model has been formulated into a non-dimensional model to facilitate systematic thermal management studies over a wide range of operating conditions. One of the key design issues is to maintain good temperature control. Finally, based on the systematic detailed and 1-D modeling studies, an integrated system optimization tool was developed. Based on the counterflow heat exchanger model as a canonical unit to represent individual components, a first-order reaction model has been implemented to calculate accurate reaction and heat generation rates. Matlab Simulink is being used to integrate a network of the various components including the ATR, WGS, and PrOx reactors, to predict the system behavior and to optimize the overall performance. The detailed component models and the 1-D models described will continue to provide submodels for individual blocks that constitute the system integration model.

**Sorbent development.** Cu-Y zeolite based sulfur sorbents have been developed and evaluated. Breakthrough curves for desulfurization of diesel for these sorbents are compared to those for several benchmark sorbents in Figure 1. Selexsorb CDX is an activated alumina specially formulated by Alcoa for the adsorption of polar organic compounds including sulfur-based molecules (mercaptans, sulfides, disulfides, thiophenes). The CuCl/γ-Al<sub>2</sub>O<sub>3</sub> sorbent was prepared by dispersing CuCl<sub>2</sub> on an activated alumina surface with the aid of a dispersing agent followed by reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>. The AC/Cu-Y sorbent is a layered bed of 15 wt% activated carbon followed by Cu-Y. The highest adsorption capacity was achieved for AC/Cu-Y. Approximately 82% of its original capacity was recovered after treatment with air at 350°C. The capacity loss could be due to modification of the carbon during calcination.

**Catalyst development.** High activity ATR, WGS, and PrOx catalysts have been demonstrated. A material consisting of 10 wt% Ni on a Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> support was identified as the best performing octane

ATR catalyst. This catalyst yielded high H<sub>2</sub> production rates under the following conditions: O/C = 1.0, H<sub>2</sub>O/C = 2.0, space velocity (SV) ~290,000 hr<sup>-1</sup> (iso-octane flow ~ 0.2 mol/hr or 100 We).

Carbide-supported WGS catalysts (M/Mo<sub>2</sub>C) were synthesized that significantly exceed important targets established by the DOE. In particular, at 240°C, conversions exceeding 90% with H<sub>2</sub> selectivities greater than 99% were achieved at gas hourly space velocities in excess of 50,000 hr<sup>-1</sup> (reactant contained 38% H<sub>2</sub>, 16% N<sub>2</sub>, 10% CO, 6% CO<sub>2</sub> and 30% H<sub>2</sub>O). Rate laws for the carbide-based catalysts are also conducive for use at low CO contents and high product concentrations. Assuming high activities, low reaction orders for the reactants and products are preferred. Table 1 compares power law reaction orders for commercial Cu/Zn/Al catalysts, two oxide supported precious metal catalysts, high surface area Mo<sub>2</sub>C and the carbide-supported catalyst.

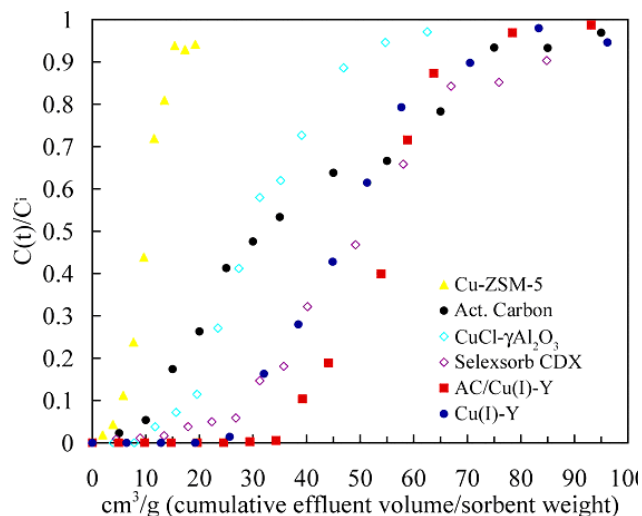
**Table 1.** Reaction Orders for the Following Power Law:  
Rate = k•P<sub>CO</sub><sup>m</sup>P<sub>H<sub>2</sub>O</sub><sup>n</sup>P<sub>CO<sub>2</sub></sub><sup>o</sup>P<sub>H<sub>2</sub></sub><sup>p</sup>

Catalyst	M	n	o	P
Mo <sub>2</sub> C	0.55±0.05	0.19±0.07	-0.02±0.06	-0.01±0.07
M/Mo <sub>2</sub> C	0.13±0.04	0.48±0.05	0.01±0.04	-0.24±0.04
Cu/Zn/Al	0.94±0.05	0.72±0.12	-0.38±0.10	-0.42±0.06
Cu/Zn/Al (1)	1.0	1.4	-0.7	-0.9
Cu/Zn/Al (2)	1.07±0.16	0.55±0.18		
Pd/CeO <sub>2</sub> (3)	0.0	0.5	-0.5	-1.0
Pt/Al <sub>2</sub> O <sub>3</sub> (4)	-0.21±0.03	0.75±0.04		

Rate data for the carbide-based catalyst were adequately described by the following Langmuir-Hinshelwood rate law where r is the rate, k is a rate constant, P<sub>i</sub> are the partial pressures and K<sub>i</sub> are the adsorption constants:

$$r = \frac{kP_{H_2O}}{(1 + K_{H_2O}P_{H_2O} + K_{H_2}P_{H_2})^2}$$

This rate law is consistent with a dual-site reaction with H<sub>2</sub>O dissociation being the rate

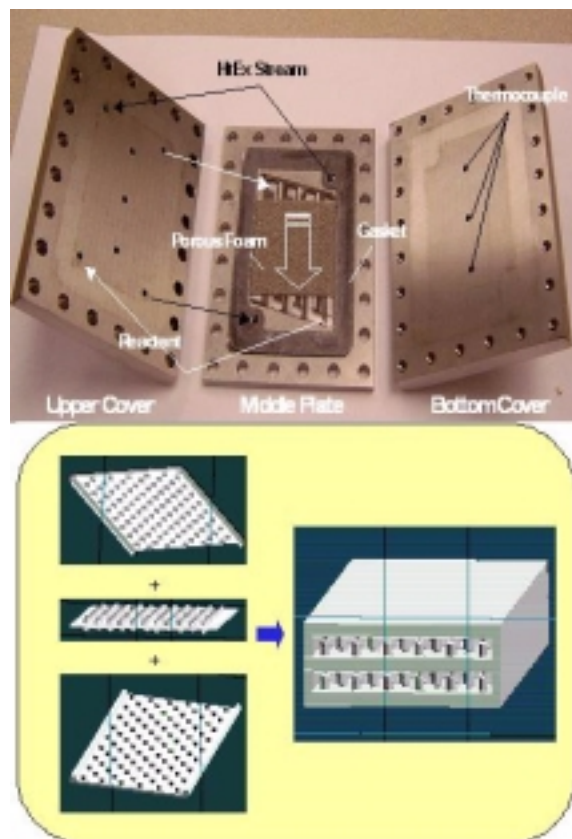


**Figure 1.** Breakthrough Curves for Desulfurization of Diesel (measurements at room temperature and atmospheric pressure)

determining step. Osram Sylvania has scaled up production of the carbide catalysts to nearly 1-kg batches.

We identified two catalysts for use in the PrOx reactor: 5% Pt/15% ceria-85% alumina and 1% Au/Fe<sub>2</sub>O<sub>3</sub>. The Pt catalyst gives greater than 98% conversion with 50% CO oxidation selectivity at high temperatures (120-180°C), and the Au catalyst gives 99% conversion with 58% selectivity at 50°C. These catalysts were wash-coated onto monoliths and silicon and aluminum micro-reactor structures. We also built honeycomb and microchannel reactors for PrOx. The honeycomb reactor was capable of reducing the CO content of ~10 L/min of reformate to less than 10 ppm.

**Microchannel System Development.** The heat required from the burner is directly coupled to the degree of heat recuperation achieved by component integration throughout the rest of the system. As a result, detailed burner/vaporizer requirements were developed based on results from the integration simulations. On a 1-kW basis, the total heat needed for vaporization and stream heating to target temperatures is 948 W, while the total heat available from the ATR and WGS reactions is 1001 W. An additional 300 W is available from combustion of the anode tailgas. A tailgas burner thus suffices for steady-state operation and is being developed. The



**Figure 2.** Illustrations of (top) Experimental Test Micro-Reactor and (bottom) Target Design Based on Simulations Results

fuel vaporizer is being developed which derives heat directly from the tailgas burner. The water vaporizer recovers heat first from the reactors and then derives additional heat from the tailgas burner or from a non-catalytic fuel burner.

Cost-effective manufacturing methods have been developed to mass produce the fuel processor components. A semi-solid forming process has been identified as one of the most promising candidate processes. This process has good capability for creating the complex micro/meso-scale geometries required for the reactor components.

## Conclusions

Significant progress was made last year. Several better performing fuel processing materials were developed. The deployment of these sorbents and catalysts should result in significant reductions in the

fuel processor size, weight and cost. Novel reactor geometries were also demonstrated. (See Figure 2.) Efforts for the coming year will focus on fabricating an integrated, 1-kWe gasoline fuel processor with characteristics that exceed key Department of Energy performance targets.

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### **FY 2003 Publications/Presentations**

1. "Autothermal Reforming of Isooctane Over Supported Nickel Catalysts", Tadd, A., Saraf, V., Schwank, J., Jundee, T., and Rirksomboon, T., Preprints, AIChE Annual Meeting, Indianapolis, IN, November 3-8, 2002.
2. "Supported Nickel Catalysts for Autothermal Reforming of Hydrocarbons", Tadd, A., Saraf, V., Schwank, J., Jundee, T., and Rirksomboon, T., North American Catalysis Society Meeting, Cancun, June 2003.
3. "High Throughput Evaluation of Novel Autothermal Reforming Catalysts for Fuel Cell Applications", Schwank, J., Tadd, A., Saraf, V., and Gould, B., EuropaCat-VI, Innsbruck, Austria, August 31- September 4, 2003.
4. "Deactivation Mechanisms for Supported Gold WGS Catalysts", Kim, C. H., Bej, S. K., and Thompson, L. T., AIChE Annual Meeting, Indianapolis, IN, November 2002.
5. "Function and Performance of Carbide Catalysts for the Water Gas Shift Reaction," Patt, J. J., and Thompson, L. T., AIChE Annual Meeting, Indianapolis, IN, November 2002.
6. "Function of Carbide and Nitride Water Gas Shift Reaction Catalysts," Patt, J. J., Bej, S. K., and Thompson, L. T., Materials Research Society Fall Meeting, Boston, MA, December 2002.
7. "Deactivation Mechanisms for Supported Gold WGS Catalysts", Kim, C. H., Bej, S. K., and Thompson, L. T., MRS Fall Meeting, Boston, MA, December 2002.
8. "Deactivation of Supported Water Gas Shift Gold Catalysts", Kim, C. H. and Thompson, L. T., ACS Spring Meeting, New Orleans, LA, March 2003.
9. "Deactivation and Regeneration of Nanocrystalline Gold WGS Catalysts," Kim, C. H., Bej, S. K., and Thompson, L. T., North American Catalysis Society Meeting, Cancun, June 2003.
10. "Desulfurization of Transportation Fuels with Zeolites Under Ambient Conditions," R. T. Yang, A. J. Hernandez-Maldonado and F. H. Yang, *Science*, 301, 79 (2003).
11. "Desulfurization of Commercial Liquid Fuels by Selective Adsorption via p-Complexation with Cu(I)-Y Zeolite," A. J. Hernández-Maldonado and R. T. Yang, *Ind. Eng. Chem. Res.*, 42, 3103 (2003).
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13. "Desulfurization of Transportation Fuels with Zeolites Under Ambient Conditions," Yang, R. T., ACS Spring Meeting, New Orleans, LA, March, 2003, Award Address of ACS Award for Separation Science and Technology.